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(21) International Application Number: PCT/FI99/00602 (22) International Filing Date: 7 July 1999 (07.07.99) (30) Priority Data: 981586 10 July 1998 (10.07.98) FI 990228 5 February 1999 (05.02.99) FI (71) Applicant (for all designated States except US): RAISIO CHEMICALS OY [FI/FI]; Raisionkuari 60, FIN-21200 Raisio (FI). (72) Inventor; and (75) Inventor/Applicant (for US only): LUUKKONEN, Kari [FI/FI]; Tenavakatu 18 A, FIN-21200 Raisio (FI). (74) Agent: OY JALO ANT-WUORINEN AB; Iso Roobertinkatu 4-6 A, FIN-00120 Helsinki (FI).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i>
(54) Title: ADDITIVE COMPOSITION FOR PAPER MAKING (57) Abstract <p>The object of the present invention is an additive composition for paper making which is added to the pulp prior to web formation in order to increase the wet strength of the web. The basic component of the composition is a component made from starch, which to its molecular weight has been thinned to a viscosity level of 10 to 400 (5 %, 60 °C, Brookfield) which by solution cationizing using a quaternary nitrogen compound is cationized to a charge of < 4 mEkv/g, the composition containing at least one additional component, such as; 1) a starch-based polymer dispersion which contains starch and a monomeric graft copolymer, which product comprises, calculated from the dry-matter content of the product; a) 5 to 40 % of starch, having a cationic charge of 0.01 to 1 and an intrinsic viscosity of > 1.0 dl/g, b) 60 to 95 % of a monomer mixture containing at least one vinyl monomer and having a film formation temperature of 0 to 70 °C of a polymer formed therefrom, and water, and/or 2) polyamide epichlorhydrin resin (PAAE).</p>		

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Additive composition for paper making

The invention concerns an additive composition for paper making to be added to fiber pulp in a step preceding the web formation step of the paper making. The additive improves essentially the strength of the wet web, which is important as regards the wet part of the paper machine, because the improved strength diminishes breaks and makes the use of higher machine speeds possible.

The basic component in the additive composition is starch, which has been modified to better meet the requirements of the invention, by reduction of its molecule size and reacting the same with a suitable nitrogen compound in order to accomplish a proper cationic charge for the starch.

The reduction of the molecule size has been effected preferably using oxidation, such as peroxide oxidation. The reduction in molecule size is preferably effected so that a starch suspension with a consistency of 5 % possesses a viscosity of 10 to 400 mPas (Brookfield), preferably 100 to 400 mPas, and most preferably 100 to 200 mPas at a temperature of 60 °C. These values can be achieved for instance using a hydrogen peroxide amount of about 0.02 to 0.3 % based on the dry-matter of the starch in mild alkaline reaction conditions. The degree of degradation aimed at depends also on the cationic charge of the end product, because an increase in the cationic charge has a lowering effect on the viscosity of the end product. A dependency prevails also between the molecule size and the cationic charge, which has an influence on the behaviour of starch on paper machine.

Starch, which is modified to a proper viscosity level is then processed with a quaternary nitrogen compound in conformity with the invention so, that it possesses a cationic charge in the range of < 4 , preferably 0.36 to 2.5, more preferably 0.72 to 1.10 mEkv/g. The product is made preferably using a solution cationizing process where the starch is introduced into the cationizing process in granular form, and the process conditions are selected to solubilize the starch totally during the process. Essential parameters for the process in this respect are the percentage of the starch to be cationized, a suitable alkalinity, and an elevated temperature. A

suitable alkaline (NaOH) charge is about 1.5 - 3 % of the dry-matter of the starch, and a suitable temperature is about 60 to 80 °C. The dry-matter content of the reation mixture should preferably be above 50 %, which i.a. gives a good yield for the end product. A suitable quaternary cationizing chemical is 2,3-epoxypropyl-
5 trimethylammonium chloride, which is to used in an amount of about 10 to 40 % of the starch.

In addition to the basic component the additive composition contains at least one further component, by means of which the properties of the basic component, which
10 are advantageous as such to the paper making process, can be modified in a direction towards the desired effect, and/or provide a composition, in which the synergistic effect of the components gives properties clearly different from the properties of the basic component.

15 One possible further component is a starch based polymer dispersion containing a graft copolymer of starch and monomers, subsequently called the graft component. This component contains, calculated as dry weight of the product, the following

a) 5 to 40 % starch having a cationic charge of 0.01 to 1 and an intrinsic viscosity
20 of > 1.0 dl/g,

b) 60 to 95 % of a monomer mixture containing at least one vinyl monomer and providing a polymer having a film formation temperature of 0 to 70 °C , and water.

25 The detailed composition of the said graft component and the preparation thereof has been explained in our copending Finnish patent application no 990229 of the same date on an invention entitled "Polymer dispersion and process for its preparation".

30 Another alternative component for the additive composition is polyamide epichlorhydrin resin (PAAE) used as a wet strength resin in the paper industry, which in the following will be called the resin component.

The additive composition can be made from these components alternatively depending on the intended use, so that either the graft or the resin component, or both, are added to the basic component.

- 5 The quantitative ratios between the basic component and the graft component can be chosen in the range of 30 to 70 / 70 to 30 %, preferably 40 to 60 / 60 to 40 %. A composition containing equal parts is especially preferred.

- 10 Correspondingly the quantitative ratios between the basic component and the resin component can vary in the ranges 25 to 75 / 75 to 25 %, preferably 40 to 60 / 60 to 40%. Also in this case a composition containing equal parts is especially preferred.

- 15 In case the additive is composed of all three components, the proportions of the components can be within the ranges:

basic component,	10 to 50 %, preferably	20 to 40 %
graft component	10 to 50 %, preferably	20 to 40 %
resin component	10 to 50 %, preferably	20 to 40 %

20

so that the composition forms 100 %.

- 25 It has been observed that advantageous results can be obtained with the additive composition according to the invention for example so that the basic component together with the graft component has led to improved retention on the paper machine. It has been observed that the printing characteristics of a paper made using this additive composition have improved, as also improved paper strength characteristics and improved dimensional stability have been observed.

- 30 The basic component and the resin component decrease the linting tendency of the manufactured paper. Improved retention and improved dewatering have been observed as advantageous effects in the manufacturing stage. It has also been obser-

ved that the additive has fixating properties, which is of importance from the point of view of removing detrimental substances from the circulation.

5 It has been observed that the strength of the wet stage web has increased especially with an additive composition which in addition to the basic component includes both a graft and a resin component.

The operability of the invention is illustrated with the following example.

10 Example 1

Newsprint was made on a pilot scale paper machine, the fiber stock of which consisted of 50 % pressure groundwood and 50 % thermomechanical pulp, which had been bleached with dithionite. In the test run, additive composition in an
15 amount of 1, 2 and 3 kg/ton paper (dry/dry) was added to the pulp prior to web formation.

The basic component in the additive composition used in the tests was thinned starch, which had been cationized using 25 %, calculated from the amount of
20 starch, of the cationizing chemical 2,3-epoxypropyl-trimethylammonium chloride.

As a second additional component, graft component, to be combined with this basic component a composition was used which contains 20 % starch, having a cationic charge of approximately 0.05 and an intrinsic viscosity of 3 to 15 dl/g, 19 %
25 acrylonitrile, 30 % butyl acrylate, 31 % styrene, and water.

As a second additional component, the resin component, polyamide epichlorhydrin resin (PAAE) was used.

30 The test results obtained are given in the table I in appendix 1 hereto.

The reference in the test was an additive, which was the same as the basic component of the additive composition according to the invention, and is indicated in the table with the symbol "15".

5 The symbol "S" in the table means an additive composition containing 50 % basic component 15 and 50 % graft component. The symbol "P" in turn means an additive composition containing 50 % of basic component and 50 % of resin component. The symbol "SP" in turn means a composition containing 1/3 of basic component, 1/3 of graft component and 1/3 of resin component.

10

The strength of the wet web was measured and based thereon the effect of the additive component on the strength was derived, by taking into account the effect of the dry-matter content of the web on the strength of the web. The relationship between the dry matter content of the web and the strength is disclosed in the graph in connection with the table I.

15

Based on the test results it can be deduced that all the compositions S, P and SP increased the strength of the wet web, of these the composition SP the best.

20

The development of the strength of the wet web as obtained from the test results is also disclosed as a graph as according to appendix 2. The symbols 15, S, P and SP correspond to the compositions defined above.

Claims

1. Additive composition for paper making to be added to the pulp prior to web formation, **characterized** in that the composition as its basic component contains a component, which is made from starch, which to its molecular weight has been thinned to a viscosity level of 10 to 400, preferably 100 to 400, most preferably 100 to 200 mPas (5%, 60 °C , Brookfield), and to its cationic charge has been cationized by solution cationizing using a quaternary nitrogen compound to a charge of < 4, preferably 0.36 to 2.5, most preferably 0.72 to 1.10 mEkv/g, and at least one additional component, which are
- 1) a starch-based polymer dispersion which contains starch and a monomeric graft copolymer, which comprises, calculated from the dry-matter content of the product
 - a) 5 to 40 % of starch, having a cationic charge of 0.01 to 1 and an intrinsic viscosity of > 1.0 dl/g,
 - b) 60 to 95 % of a monomer mixture containing at least one vinyl monomer and having a film formation temperature of 0 to 70 °C of a polymer formed therefrom, and water,
 - 2) polyamide epichlorhydrin resin (PAAE).
2. The additive composition according to claim 1, **characterized** in that the quantitative ratios between the basic component and the component 1) are in the range of 30 to 70 / 70 to 30 %, preferably 40 to 60 / 60 to 40 %, most preferably being in equal parts.
3. The additive composition according to claim 1, characterized in that the quantitative ratios between the basic component and component 2) are in the range of 25 to

75 / 75 to 25 %, especially 40 to 60 / 60 to 40 %, most preferably being in equal parts.

4. The additive composition according to claim 1, **characterized** in that the quantitative ratios between the basic component and the components 1) and 2) are in the range

	basic component,	10 to 50 %, preferably	20 to 40 %
	graft component	10 to 50 %, preferably	20 to 40 %
10	resin component	10 to 50 %, preferably	20 to 40 %

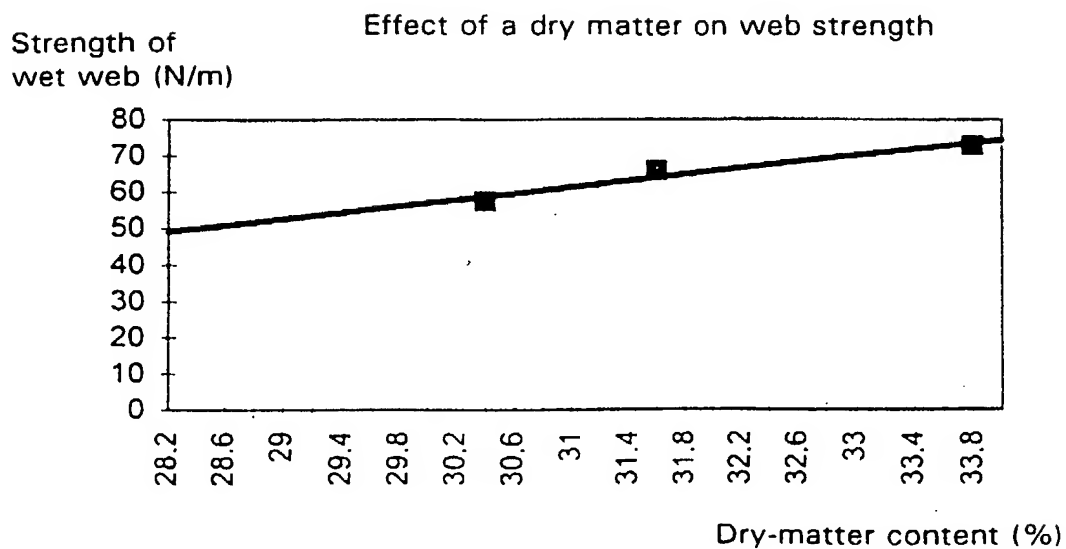
so that the composition forms 100 %.

Figure 1

App. 1

Table 1

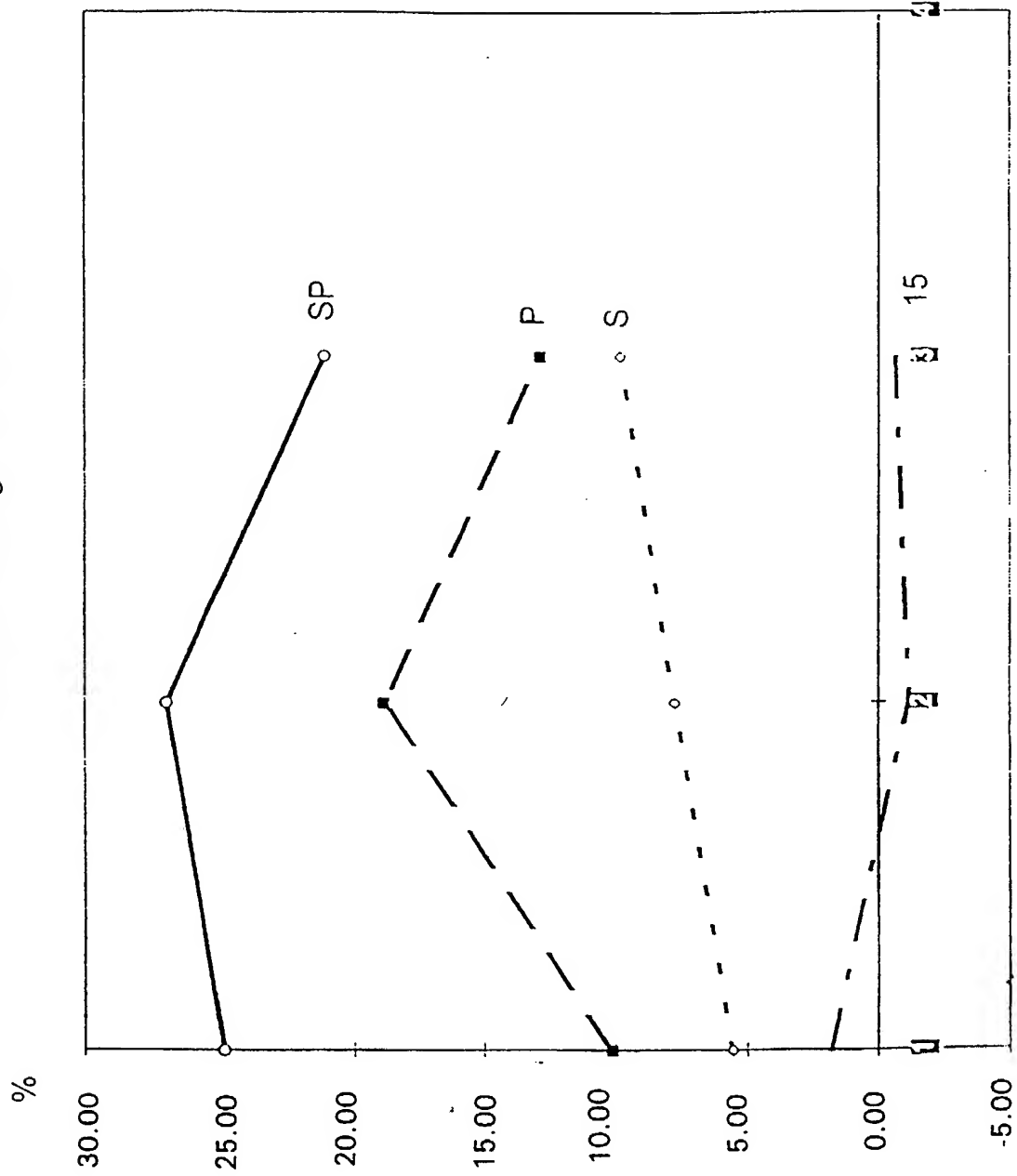
Additive	Dose (kg/t)	Dry-matter content (%)	Strength of wet web N/m	Effect of additive, N/m
15	1	31.6	65.73	1.83
15	2	30.4	57.51	-1.18
15	3	33.8	72.81	-0.64
S	1	33.6	78.14	5.55
S	2	29.9	64.27	7.75
S	3	29.6	65.08	9.86
P	1	28.2	59.22	10.08
P	2	30.0	75.82	18.86
P	3	29.3	66.79	12.87
SP	1	27.8	72.41	24.83
SP	2	25.0	62.11	27.04
SP	3	26.1	60.99	21.10



SUBSTITUTE SHEET (RULE 26)

App. 2

Increase in strength of wet web



Dose, kg/t

Figure 2

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 99/00602

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: D21H 17/29, D21H 17/46, D21H 21/20
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	GB 1095123 A (EASTMAN KODAK COMPANY), 13 December 1967 (13.12.67) --	1-4
Y	WO 9746591 A1 (GEORGE WESTON FOODS LIMITED), 11 December 1997 (11.12.97) --	1-4
A	WO 9716595 A1 (WEYERHAEUSER COMPANY), 9 May 1997 (09.05.97), the claim --	1-4
A	DE 19728789 A1 (BAYER AG), 7 January 1999 (07.01.99), page 5, lines 56-58 --	1-4

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0301372 A1 (BASF AKTIENGESELLSCHAFT), 1 February 1989 (01.02.89) --	1-4
A	WO 9310305 A1 (RAISION TEHTAAT OY), 27 May 1993 (27.05.93) -- -----	1-4

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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WO 9746591 A1	11/12/97	AU 2758997 A AU P0017196 D	05/01/98 00/00/00
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WO 9310305 A1	27/05/93	AT 157132 T DE 626022 T DE 69221735 D,T DK 626022 T EP 0626022 A,B SE 0626022 T3 ES 2106200 T FI 91428 B,C FI 915310 A US 5578169 A	15/09/97 11/09/97 26/03/98 23/03/98 30/11/94 01/11/97 15/03/94 12/05/93 26/11/96

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